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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

IV. THE CAUSE OF DETONATION OR COMBUSTION KNOCK IN ENGINES

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CANADA

Reprinted from the
CANADIAN JOURNAL OF RESEARCH
F, 26 : 228-240 : 1948.

MAY 18 1960

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11 May, 1960

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106-04306/

Reprinted from Canadian Journal of Research, F, 26 : 228-240. May, 1948
Published by the National Research Council of Canada

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IV. THE CAUSE OF DETONATION OR COMBUSTION KNOCK IN ENGINES[1]

By R. O. King[2]

Abstract

A nuclear theory of self-ignition is described which is based on the substitution of finely divided carbon for the nuclear drops of the Callendar theory. The finely divided carbon appears in the gaseous combustible mixture in the engine as a result of pyrolysis of the lubricating oil or of the fuel. The theory is therefore of general application and can be applied to explain combustion knock or detonation when permanent gases such as hydrogen as well as hydrocarbon vapors are used as fuel for the carburetor type of internal combustion engine. The theory is supported by experimental evidence quoted mainly from earlier publications and is intended as a working hypothesis for further confirmatory experiments.

Introduction

The experiments described in preceding Parts were directed mainly to ascertain the cause of the effect of metallic dopes to delay the onset of detonation in engines. They support the view that delay or prevention is due to dilution of the end gas by the products, steam and carbon dioxide, of an oxidation reaction occurring on the surface of the combustion space made 'active' by metal deposited on the thermal decomposition of the dope. The detonation delaying effect of dilution would operate whatever the cause of detonation, and discussion of that effect was therefore withheld pending a description of especially related experiments. Some of the experiments have been completed and others are in progress. It is hoped to described all of them in succeeding Parts. It will, however, be of assistance to the reader and save space later if the working hypothesis used to plan the experimental work is given separately in this Part after a brief review of recent theory.

Section I

The Callendar Nuclear Theory of Self Ignition

The continued propagation of flame in a combustible mixture after ignition at a point depends, according to the classical theory, on the rate of heat generation by combustion continuing to be greater than the rate of loss by conduction, convection, and radiation. The theory does not provide an adequate explanation for the sudden increase in flame velocity in a tube after a certain distance has been traversed by the flame front or the similar effect in the combustion space of an engine. In fact, ignition of the unburned gas well ahead of the flame front, that is, self-ignition, can be obtained in

[1] *Manuscript received January 17, 1948.*
Contribution from Defence Research Board, Ottawa, Canada.

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suitable conditions of temperature and pressure. Self-ignition of the end gas in an engine results in detonation, indicated by combustion knock which occurs also if the rate of flame propagation become abnormally great.

A nuclear theory of self-ignition was advanced by Callendar (7, 8) to explain the occurrence of detonation in an engine and the antiknock effect of metallic dopes. In the particular case of ordinary liquid hydrocarbon fuels, always containing some proportion of high boiling point constituents, it was considered that the nuclei would be liquid drops of the higher boiling point fractions remaining after evaporation of the lighter fractions of the fuel. These residual drops, as they evaporate, would be contained within a shell of nearly pure vapor which would recondense in part as the compression pressure was raised because hydrocarbon vapor, unlike steam, tends to condense on compression. Vaporization would thus be retarded and the drops could persist until late in the period of combustion. The drops, being surrounded by vapor of the high boiling point constituents of the fuel, would have a lower ignition temperature than that of the gaseous mixture in which they were dispersed. Thus if the end gas were impregnated with liquid drops, nearly simultaneous ignition (detonation) might occur prior to the completion of combustion of the gas in the normal course of flame travel.

Hydrocarbon fuels completely vaporized and mixed with air in combining proportions present some difficulties because condensation during compression could not occur in the circumstances. Callendar suggested that in such cases the smoke particles which are always present in the operation of an internal combustion engine would serve as foci of condensation and "with the aid of such carbon nuclei, drops of a highly ignitable nature may continue to exist or *may be formed by condensation* at temperatures such that the mixture should be completely vaporized according to the ordinary rules of calculation."

The possibility that carbon nuclei as such might be effective centers of ignition in an otherwise homogeneous gaseous combustible mixture was not discussed. The carbon nuclei mentioned as being present in the engine combustion space were the smoke particles remaining from the previous combustion of hydrocarbons, and it was suggested only that they could promote the *formation of liquid drops* in a completely vaporized mixture by serving as foci of condensation.

Aside from the failure of the nuclear drop theory to account for detonation in completely vaporized mixtures, there appeared to be some doubt about the drops being present in sufficient concentration in the end gas to provide an igniting effect, and Callendar's suggestion that the metallic dope prevented ignition of the drops by plating them with metal, thus preventing absorption of radiation from the flame, was not convincing. The chemical side of the problem was therefore explored at his request but with the fixed idea that some product of the oxidation of the rich mixture surrounding the slowly evaporating drops would be readily inflammable and thus ignite the drops.

Oxidation, according to the Armstrong–Bone hydroxylation theory, then generally accepted, would begin with the formation of an alcohol and proceed by further oxidation to aldehyde, carbon monoxide, steam, and carbon dioxide. All the oxidation products mentioned, except the aldehyde, were known to delay detonation. A number of aldehydes were tried as additions to engine fuel but proved to be of inappreciable effect on detonation (5, p. 183; 6, p. 20). The idea that detonation must be due to the accumulation of some oxidation product in the nuclear drops was however not abandoned. It was known that certain unstable organic peroxides decomposed with some violence on heating, and it was suggested (by Mardles) that a peroxide instead of an alcohol might be the primary oxidation product. The suggestion fitted exceptionally well into the nuclear drop theory, and, as the result of numerous confirmatory experiments, Callendar concluded (5, 6), in respect of *paraffinic fuels and ether*, that although the amount of peroxide formed would not in itself be sufficient to cause the detonation observed it would act as a primer for the simultaneous ignition of the nuclear drops—and detonation thus caused would be prevented if metallic dope were concentrated in the drops owing to the reduction of the peroxide by the metal of the dope.

It will be noted that the nuclear theory remained encumbered by liquid drops and, although it could not be accepted as having more than a limited field of application, the idea that organic peroxides were responsible in some way for fuel detonation in engines received fairly general approval in large part because it seemed to pave the way for the application of chain reaction theories to combustion as it occurs in the engine.

Section II

Chain Reaction Theory

A nonhomogeneous combustible mixture is a necessary prelude to self-ignition, according to the nuclear theory. The chain reaction theory was devised to account for oxidation leading to ignition in a homogeneous mixture, reaction being between single molecules. Experimental evidence in support of the theory has been generally obtained by using reacting mixtures not diluted with nitrogen, at relatively low pressures and without taking flow configuration (15) into account. Nevertheless many attempts have been made to use the theory to explain the mechanism of oxidation and detonation in the turbulent fuel–air mixtures used in engines at the extremely high pressures attained during combustion of the end gas, although mixtures so diluted with nitrogen cannot be detonated in tubes.

There is little agreement about the manner of initiation of chain reactions and still less about the mechanism of the reaction. It is most simple to suppose, as suggested by Mardles (5, 6) and by Moureu, Dufraisse, and Chaux (18), that a collision between a fuel and an oxygen molecule results in the formation of a peroxide having a relatively high energy content, and Egerton (9) considers that reactivity is handed on from the peroxide to new reactant

molecules, the reaction being autocatalytic in character, a view that is not in accordance with the Armstrong–Bone hydroxylation theory in support of which there is considerable experimental evidence if reaction occur at high pressure. Egerton considers that the metallic antiknocks delay oxidation by forming metallic peroxides that react with and destroy the fuel peroxides, thus breaking the reaction chains and preventing detonation.

Norrish (19) considers the peroxidation theory to be unsatisfactory and suggests that reaction chains start from the aldehyde and proceed by an "atomic chain" mechanism according to which methane for example would be oxidized by a chain reaction involving free radicals and atomic carbon. Oxidation of other hydrocarbons requires atomic oxygen as a link in the chain reaction. Norrish, to a considerable extent, avoids conflict with the hydroxylation theory of oxidation but does not, in the reference given, apply his chain reaction theory to explain the action of metallic antiknocks.

Rice (21) considers that thermal decomposition results in the replacement of one molecule of hydrocarbon by several, with the result that the increase in concentration may greatly augment rate of oxidation and increase knocking tendency accordingly, oxidation being a chain reaction involving free radicals. Metallic antiknocks are assumed to cause the fuel molecule to decompose into relatively few small molecules and in this way reduce knock. Rice appears to envisage a limited decomposition, unlike Norrish who assumes decomposition to carbon or oxygen atoms.

Steele (23) suggests that hydrogen liberated by the decomposition of hydrocarbons during the combustion period in the engine is responsible for fuel knock. He considers this view to be supported by the engine experiments of A. F. Burstall showing that hydrogen gives rise to violent knock (4) while carbon monoxide does not knock in any circumstances (3). It is further suggested by Steele that the knock due to hydrogen liberated by decomposition of the hydrocarbon can be prevented by adding more hydrogen to carry the partial pressure out of "a critical range."

Boerlage and Van Dyck (1) established a relation between the *initial* cracking speeds of Diesel engine fuels and the cetene numbers with a considerable degree of success. An attempt to establish a relation between the *initial* cracking speeds of fuels used with carburetor engines and octane numbers was less successful. The initial cracking speed of iso-octane which is at the top of the octane scale was, for example, greater than that of heptane which is at the bottom of the scale. The initial cracking speed of heptane was however greater than that of some hydrocarbons of a higher octane rating. The experiments were made at atmospheric pressure and conditions were not the most suitable for cracking the hydrocarbons to carbon. The experimenters assumed that detonation depends on a high rate of oxidation in a homogeneous mixture of hydrocarbon vapor and air, and were most concerned with the gaseous products of cracking in an endeavor to determine the conditions in which free radicals or an active form of oxygen would be present and initiate chain reactions.

The above brief review of chain reaction theory as applied to combustion in the engine is admittedly superficial. It has been given to illustrate in some degree the difficulties met with in applying the theory to explain the cause of detonation in an engine and the action of antiknocks. The metallic antiknocks decompose at temperatures reached before the end of compression and the metal, which is generally agreed to be the active agent to prevent knock, is deposited mainly on surfaces. It is difficult to understand how this metal can be present later on to break reaction chains in the end gas. Similarly it is difficult to understand how organic peroxides, which by definition are initial and unstable products of slow oxidation at relatively low temperatures, can persist and be essential links in chain reactions occurring at the extremely high temperatures of the end gas. The Callendar nuclear drop theory did at least provide a means of their persistence. Finally, Egerton in a lengthy discussion of "Existing knowledge on knocking and its prevention" (10), states "although it would be generally agreed that in the oxidation of saturated paraffins, reaction chains are operative, there is as yet no agreement on the mechanism of the process or the nature of the chain carriers."

Section III

Heterogeneous Oxidation Reactions and a Revised Nuclear Theory of Self-Ignition

Outline of Theory

The experiments described in preceding Parts indicate that flameless oxidation of fuel in mixtures with air in engine conditions occurs solely on hot surfaces, not in the body of the gas by a chain reaction process. The surfaces in the combustion space of an engine may comprise areas of metal, metallic oxides, adherent carbonaceous matter, or carbon distributed in the combustible mixture as fine particles. When the surfaces reach a suitable temperature oxidation may be to partial or final products in accordance with the nature of the surfaces and the degree of turbulence. The heat of reaction does not suffice to start a flame if surface temperature is controlled by water or air cooling, and combustion after spark ignition proceeds to completion without the occurrence of pre-ignition or detonation. It is to be noted that the temperature of containing surfaces can be controlled but not that of the surfaces of material nuclei in the body of the gas.

Flame may, however, be started without spark ignition if a surface become so thickly coated with carbon that external cooling is ineffective or if insufficiently cooled points or small areas become incandescent. Flame may also be started by the combustion of aldehydes which are formed in great profusion in conditions of excessive turbulence, and can be ignited by contact with surfaces at the temperature attained in high duty engines by the exhaust valve. Thus methyl and ethyl alcohols, which oxidize in the first stage to aldehydes, are especially prone to pre-ignition when used as engine fuel for the Ricardo E35 engine in spite of the cooling effect arising from the high latent heat of evaporation.

Flame started in any of the ways mentioned moves through the combustible mixture just as if it had been started by an electric spark and does not give rise to detonation. If the flame starts before the passage of the spark it is described as pre-ignition and if timing is approximately correct the engine will run without spark ignition.

Detonation as it occurs in an engine using hydrocarbon fuel can be initiated solely if flame be started nearly simultaneously at points distributed throughout the end gas, and experiments indicate that the conditions required are governed by the temperature and pressure of the gas and the concentration in it of carbon nuclei, the concentration being determined, other things being equal, by the pressure. The theory will now be discussed in greater detail.

End Gas Temperature and Pressure

The temperatures and pressures attained by the end gas at compression ratios extending from 4 to 10 : 1 given in Table I below are calculated on the basis that detonation occurs when the combustion pressure reaches 90% of the maximum value.

TABLE I

END GAS TEMPERATURES AND PRESSURES, RICARDO E35 VARIABLE COMPRESSION ENGINE

Compression ratio	Initial compression pressure	Initial compression temperature, ° C.	90% of max. combustion pressure, lb./sq. in.	Calculated temperature of end gas, ° C.
4 : 1	Atmospheric	133	346	673
5 : 1	"	112	477	707
6 : 1	"	102	616	741
7 : 1	"	95	—	765
8 : 1	"	90	—	809
10 : 1	"	—	—	877

The data used to compile the table are from published performance figures in respect of the Ricardo E35 variable compression engine (5, p. 211; 6, p. 26; 20). The end gas temperatures were calculated taking the value of γ to be 1.36. This allows for the end gas receiving some heat during the combustion period. If the temperature at the end of compression by the piston were required, the value of γ would be taken to be 1.34. The end gas temperatures for compression ratios of 7 to 10 : 1 are extrapolated values, indicator diagrams not being available. It will be noted that end gas temperature is very nearly a linear function of compression ratio, and, evaluating the constants, — end gas temp. = $(34 \times \text{C.R.} + 537)$° C.

Nuclear Ignition

The Callendar theory of self-ignition was based on the nuclei, dispersed in a combustible gaseous mixture, having a lower ignition temperature than the otherwise homogeneous gas (7, 8). It was, however, shown by the later experiments of King (16) and King and Mole (17) that the nuclei need not

be of a combustible substance. Fine drops of water, stone dust, or powdered metallic oxides are all effective explosion agents. A description of experiments showing the igniting effect of a variety of nuclei in respect of mixtures of hydrogen, ethylene, and methane is given in the references quoted. Similar igniting effects were obtained at the time, in respect of carbon monoxide and acetylene. Experiments made later, with the arrangement of apparatus described in the references, in the Colloid Science Department, Cambridge University, demonstrated that pentane–air mixtures were especially sensitive to ignition by nuclei. When the mixture was supplied to the combustion tube at the rate of 300 cc. per min. explosion occurred at 570° C., but nuclei such as finely divided silica caused explosion at 450° C. and the still lower explosion temperature of 350° C. was observed when the nuclei were fine particles of nickel oxide. Carbon was found to be an effective igniting agent but the variety used was so finely divided that the particles tended to stick together and float about instead of falling rapidly through the heated mixture. The cause of the effect is still a subject of speculation but there are two possibilities, one chemical, the other electrical. A reasonable chemical explanation is that the nuclei provide surfaces in the gas on which oxidation can occur, with the consequence that the heat of reaction would raise the temperature sufficiently to start a flame. It is difficult to apply this explanation to a particle of water, which would be evaporated to steam in the process. An electrical explanation seems to apply better to drops of water. It is known that such drops become positively electrified when falling through air even at atmospheric temperatures, and the potential of the charge would increase as the surface area decreased as evaporation proceeded. It is not impossible that ignition is electrical in some cases and due to the heat of chemical reaction in others. However, considering combustible nuclei such as carbon particles which, as will be shown in a subsequent Part, are especially effective to ignite combustible gaseous mixtures, it is reasonable to suppose that flame is started by the heat of the oxidation reaction even if the hot carbon particles which are pyrophoric, are themselves insufficient. Thus, with reference to Table I, the temperature of the end gas late in the period of combustion in an engine exceeds 600° C. even at the low compression ratio of 4 : 1. Carbon particles derived from cracking of hydrocarbon fuel would be red hot in the circumstances and tend to start a flame in most combustible mixtures even if temperature were not further increased by oxidation of the gas in contact with them and by radiation from the advancing flame. At the relatively high compression ratio of 6 : 1 temperature in the end gas exceeds 700° C., Table I, and the carbon particles would be in an active state of combustion.

Carbon Formation in the Engine Combustion Space

Pyrolysis of the lubricating oil yields free carbon. The carbon may be contained in part in sticky substances tending to adhere to surfaces and in part as fine particles which appear in the exhaust when the lubricant passes the piston at an excessive rate. The extent of the formation of adherent

carbonaceous matter, rather than of free carbon distributed throughout the combustible gaseous mixture, depends on factors such as the natures of the lubricant and of the fuel as well as mixture strength. Free carbon derived from the lubricating oil would be distributed throughout the whole of the combustible mixture, not especially concentrated in the end gas. Detonation is therefore not attributed to ignition by such carbon nuclei. They may, however, act to increase rate of flame propagation.

A second source of free carbon is found in the cracking of fuel molecules in the flame front. Thus Haslam and Russell (14), referring to the combustion of hydrocarbons, state that "under ordinary combustion conditions there is a race between thermal decomposition or "cracking" and the process of hydroxylation (oxidation). If the conditions favor oxidation there will be no soot. On the other hand if the conditions favor cracking the hydrocarbon will decompose into carbon and hydrogen and will burn with a smoky flame." The conditions in the engine favor cracking. Thus the flame as it moves through the combustible mixture, impinges on relatively cool surfaces and the formation of soot would be expected. The conditions are in fact similar to those used to procure 'acetylene black' from the burning gas, and it is significant that although the molecule of acetylene is thermally stable at end gas temperatures when the gas is diluted with nitrogen (22), yet the gas cannot be used as engine fuel even at low compression ratios because of the violence of detonation. It may be concluded therefore that free carbon is carried into the end gas by the turbulence which always accompanies the movement of flame and provides the distributed ignition centers required for detonation.

The third source of free carbon, namely the cracking of the end gas, provides ignition nuclei just where required to promote detonation. There is however little information available in respect of the rate of carbon formation when pentane and other hydrocarbons usually present in fuel for carburetor engines are decomposed at the temperatures and pressures of the end gas as given in Table I. It was observed by Callendar and associates (5, 6) that the combustion of paraffins ranging from pentane to undecane was accompanied by a fine persistent fog, some of which passed through the train of absorption apparatus. Similar effects were observed during later experiments and quoting from notes made at the time and referring to the combustion of pentane "Both oxidation and decomposition became appreciable at 300° C. A feature is that decomposition is delayed if oxidation proceed rapidly but on the other hand a rapid rate of decomposition as indicated by the volume of smoke issuing from the combustion tube is a sure indication of a slow rate of oxidation." It appears therefore that the relation between hydrocarbon oxidation and decomposition reactions in flameless combustion is similar to that described by Haslam and Russell in respect of combustion in a flame, as already mentioned.

Decomposition of the paraffins lower than pentane was carried out by Hague and Wheeler (13) in a silica vessel at the temperature of 950° C. Methane, which is a non-knocking fuel, yielded a trace only of carbon. Ethane, propane, and butane yielded, respectively 13.9, 11.3, and 19.6% of carbon. The initial cracking temperature of butane was found to be 435° C., and it may be concluded that the higher paraffins used as engine fuel begin to decompose at still lower temperatures to yield some proportion of free carbon.

Egloff (11) states that the thermal decomposition of pentane has been meagerly investigated but that slow decomposition seems to begin below 400° C. and refers to the "ever present carbon." Similar comment is applicable to hexane.

In view of the lack of data in respect of the pyrolysis of the liquid hydrocarbons commonly used as engine fuel, it is fortunate that especially useful results having a direct bearing on the validity of the nuclear theory of ignition were obtained incidentally by Tizard and Pye (24) during experiments on the ignition of such hydrocarbons by sudden compression. The experiments were directed toward measuring the delay period before ignition and explosion would occur in a hydrocarbon–air mixture compressed to a temperature such that ignition would occur eventually. It was always found that, when an explosion was sharp, combustion was not complete, a fluffy deposit of carbon being thrown down although oxygen was in considerable excess.

The question at issue so far as the nuclear theory is concerned is what came first, decomposition to form ignition nuclei of finely divided carbon or ignition due to a homogeneous oxidation reaction. The question seems to have been answered by the experimental results. Thus the delay period was shortened if, by lack of preliminary cleaning, finely divided carbon was already present in some concentration. Moreover, it is generally agreed that the combustion of hydrocarbons does not involve the preferential oxidation of the hydrogen in the molecule and, accordingly, the carbon found by Tizard and Pye was due to the fact that pyrolysis preceded ignition.

Relatively low temperatures of ignition by compression were observed, values depending on whether ignition temperature were taken as the maximum that had been attained by some part of the compressed mixture or the estimated mean temperature. The mean values for pentane, hexane, heptane, and octane, respectively were 336°, 306°, 292°, and 275° C. Thus, all the paraffin hydrocarbons tried yielded finely divided carbon by pyrolysis at or below the temperatures mentioned.

Higher members of the paraffin series beginning with gas oil are commonly used as cracking stock. Carbon formation was especially troublesome in early methods. Brooks (2, pp. 2078-2087), referring to the Burton process by which the cracking of gas oil or other distillates was carried out at temperatures of about 420° C. and pressures of about 95 lb. per sq. in., states that after treatment of every batch it was necessary to open the still and scrape the carbon off the bottom.

Characteristics of Knocking Combustion as Shown Photographically by Withrow and Rassweiler (25)

The photographs of successive stages of combustion in an engine were taken by a high speed camera developed in the Research Laboratories Section of General Motors Corporation. A set of 30 of the pictures showing knocking combustion is reproduced as Fig. 1 from prints off the original negatives, supplied by Dr. T. A. Boyd, Head of the Fuel Research Section. The pictures are shown in the order taken, reading from left to right and down, starting at 29° before and finishing 40.6° after top dead center (T.D.C.). The engine speed was 900 r.p.m., the compression ratio 4.7 : 1, and the fuel a gasoline having an octane number of 48. The photographs were taken through a flat fused quartz plate 0.75 in. thick covering the combustion chamber which was therefore a non-turbulent type and most suitable for observations of orderly flame movement. It is of interest to interpret the characteristics of combustion shown by the photographs in the light of the revised nuclear theory of ignition stated in preceding paragraphs.

The igniting spark appears at 24.2° before top dead center but flame is not easily visible until 7.2° later. It spreads rapidly during the period 14.6° to 2.6° before top dead center apparently on the carbon nuclei necessarily present in the combustible mixture, and the consequent speckled appearance with the growth of bright spots is the outstanding feature of the period. A change to solid luminescence then begins and is complete at 2.2° after top dead center. That is, 19.2° of crank angle, a time interval of 0.00356 sec. at 900 r.p.m., has been required for the propagation and building up of flame to the stage of solid luminescence. The time interval would be 0.00485 sec. if taken from the passage of the spark.

The temperature and pressure of the unburned gas ahead of the flame front has been increasing during the time interval mentioned above and also the concentration of carbon nuclei. Auto ignition in the end gas is obtained accordingly and shows in the picture taken 0.2° before top dead center near the end of the combustion space over the piston and separated from, and as far ahead of, the flame front as is possible in the confined space. The next picture taken less than 0.0005 sec. later shows that spontaneous combustion has occurred through the whole of the end gas except for a very small area lying just ahead of the flame front. The picture next in order shows the end gas completely filled with flame again of a speckled appearance as would be expected according to the nuclear theory.

It is of interest that the burning mixture ahead of the flame never exhibits the solid luminescence characteristic of the final stage of combustion behind the flame front. A speckled appearance persists, indicating that combustion of the carbon particles responsible for detonation is not completed, and, as would be expected, puffs of black smoke are seen in the exhaust of an engine on the occurrence of detonation knock as distinct from combustion knock.

Furthermore it is well known in engine practice that a non-knocking 'correct' mixture burns with a nearly colorless flame and that it becomes white and luminous if detonation occur. Withrow and Rassweiler, for example, found it necessary to use a considerable proportion of benzene in the fuel mixture in order to obtain photographs of a non-knocking combustion or of the flame movement prior to knock.

Another matter of interest is the incandescent carbon appearing in bright patches mainly around the inlet valve, top left-hand corner of the pictures. It can be seen first in the picture taken at 14.2° after top dead center and continues to glow throughout subsequent pictures, remaining incandescent after combustion of the gaseous mixture is substantially complete.

It is also of interest to compare the explosion times in an engine combustion space with those observed by Fenning for explosions in a bomb (12). The bomb was cleaned between explosions by blowing out with air and there was of course no lubricating oil. There would therefore be no carbon nuclei in the combustible mixture at the time of ignition by the spark, and such nuclei as would be formed by pyrolysis of the hydrocarbon would not appear until late in the explosion period. In the circumstances the period of time between the passage of the spark and the attainment of maximum pressure when using a nearly 'correct' air–petrol mixture was 18 times that observed by Withrow and Rassweiler in the engine combustion experiments just described. Moreover Fenning did not obtain detonation until the mixture was made overrich in petrol, 10.7 to 1, air–petrol, a circumstance promoting the formation of carbon by pyrolysis in the mixture ahead of the flame. The explosion time could not then be observed because the indicator mirror was knocked off the pivots. However, in a 12.9 to 1 air–petrol mixture which just did not detonate, the explosion time was 0.0682 sec. as compared with the 0.0780 sec. observed when the mixture was nearly 'correct'.

The relatively long explosion time in a bomb is usually attributed to the degree of turbulence in the mixture being less than in engine conditions, but in the Withrow and Rassweiler experiments the engine speed was 900 r.p.m. only, the combustion space was not of a turbulent type, and the photographs do not show any mass movement of the burning mixture until late in the combustion period. The conclusion is that the extremely high rate of flame propagation in an engine is due in large part to the carbon nuclei necessarily present throughout the combustible mixture.

Conclusions

The revised nuclear theory of self-ignition, which substitutes carbon particles due to pyrolysis for the liquid drops of the Callendar theory, is complementary to the revised theory of surface oxidation developed in Parts I, II, and III to account for the effect of metallic antiknocks to delay or prevent detonation in carburetor engines using hydrocarbon fuels. Thus the

PLATE

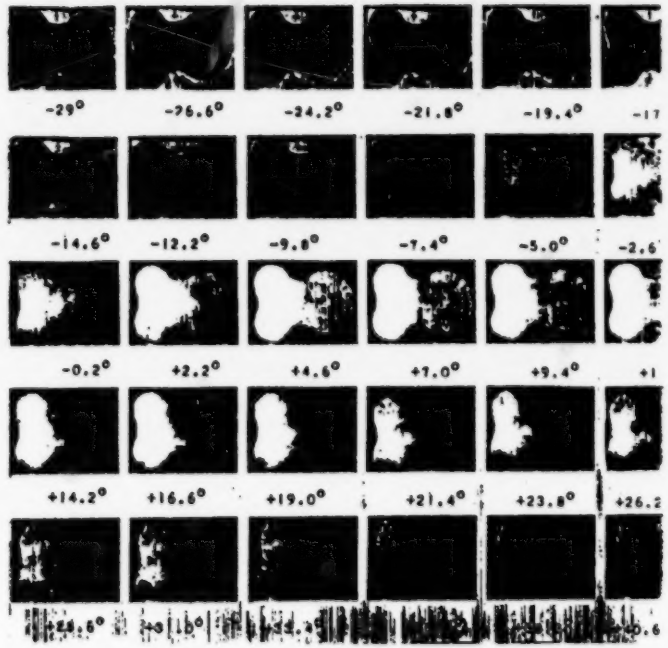

FIG. 1. *Photographs of knocking combustion in an engine, taken by Withrow Rassweiler over the period 29° before to 40.6° after top dead center at intervals of 2. crank angle, engine speed 900 r.p.m.*

unburned mixture ahead of the flame is subjected simultaneously to pyrolysis and to oxidation on the contact surfaces. The extent of the heterogeneous oxidation reaction and the nature of the products depends on the degree of turbulence in the mixture, the nature and temperatures of the surfaces, and the combustible mixture. The products of the reaction may be aldehyde, carbon oxides, and steam in varying proportions and are carried into the body of the end gas by turbulence and can be detected therein by chemical or spectroscopic methods of analysis. The end gas, diluted accordingly, tends to become noninflammable by finely divided carbon when the nature and temperature of contact surfaces are such that steam and carbon dioxide constitute a large proportion of the products of the heterogeneous reaction. That is, whether or not detonation occur in particular conditions depends on the result of a race between pyrolysis and a heterogeneous oxidation reaction. Detonation may be described in popular terms as differing from the familiar dust explosion solely in that the combustible dust is distributed in an ignitable mixture of air and gaseous fuel instead of in air only.

Acknowledgments

The constructive criticism of Dr. E. W. R. Steacie, National Research Council, and of Dr. George F Wright, University of Toronto, has been of assistance in the preparation and revision of this paper.

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167,117